

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 255 238 B1

(12)

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: **30.12.92** (51) Int. Cl.⁵: **B65D 65/40, B32B 27/08**
(21) Application number: **87305792.1**
(22) Date of filing: **30.06.87**

(54) Inter-ply adhesion between vinylidene chloride copolymers and linear ethylene copolymers.

- (30) Priority: **30.06.86 US 880258**
24.06.87 US 65987
(43) Date of publication of application:
03.02.88 Bulletin 88/05
(45) Publication of the grant of the patent:
30.12.92 Bulletin 92/53
(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE
(56) References cited:
US-B- 237 953

- (73) Proprietor: **W.R. Grace & Co.-Conn. (a Connecticut corp.)**
Grace Plaza 1114 Avenue of the Americas
New York New York 10036(US)
(72) Inventor: **Garland, Steven Brent**
104 Grande Oaks Ct.,
Simpsonville, South Carolina 29681(US)
Inventor: **Ferguson, Daniel Joseph**
4743 Warden Drive
Spartanburg, South Carolina 29301(US)
(74) Representative: **Collier, Jeremy Austin Grey et al**
J.A.Kemp & Co. 14, South Square Gray's Inn
London WC1R 5EU(GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Descripti n

FIELD OF THE INVENTION

5 This invention relates to a method of improving the adhesion between a layer of vinylidene chloride copolymer and a layer of a linear ethylene/alpha-olefin copolymer and to the film produced thereby. More particularly, the invention relates to heat shrinkable films having a barrier layer of vinylidene chloride copolymer and a layer of linear low density polyethylene or very low density polyethylene and to a method for increasing the adhesion between the layers and thereby decreasing the incidence of delamination.

DEFINITIONS AND ABBREVIATIONS

As used herein, the terms and abbreviations set forth below will be understood to be defined as stated:

LLDPE is an abbreviation for linear low density polyethylene and refers to copolymers of ethylene
 15 having: (1) a higher-alpha-olefin such as butene, octene, hexene, etc. as a comonomer; (2) a density of from 0.910 to as high as 0.935 grams per cubic centimeter; (3) molecules comprising long chains with few or no branches or cross-linked structures; and, (4) being produced at low to medium pressures by copolymerization using heterogeneous catalysts based on transition metal compounds of variable valance.

VLDPE is an abbreviation for very low density polyethylene and refers to copolymers of ethylene
 20 having: (1) a greater proportion of higher alpha-olefin as a comonomer, in general, than LLDPE; (2) a density of 0.910 to 0.86 or lower; (3) little low temperature embrittlement; and, (4) then produced by a catalytic, low pressure process at a pressure of no greater than 7,000 KPA.

Saran or PVDC refers to copolymers of vinylidene chloride in which the vinylidene chloride monomer comprises at least 51% of the copolymer. Generally, saran is desirable as a layer in multi-layer thermoplastic film constructions because of its oxygen barrier properties.

EVA refers to copolymers of ethylene and vinyl acetate. The vinyl acetate content may range from a low of 2 or 3% to a high of 30 or 40% depending upon the desired properties.

EBA refers to ethylene/butyl-acrylate copolymer and the butyl-acrylate monomer content may vary from as low as 2% to 18% or higher by weight.

BACKGROUND

Heat shrinkable polymeric films are widely used for packaging of fresh and processed meats, cheeses, poultry and a large number of non-food items. Some of the films are formed into heat shrinkable bags or
 35 pouches which are supplied to the meat packer.

Processing and distribution requirements demand that the film and bags made therefrom have a wide range of difficult-to-meet properties. Of great importance to the packer is the capability of a bag to survive physically the process of being filled, evacuated, sealed, heat shrunk, and shipped to various distribution points. The bag must be strong enough to survive the material handling and also physically protect the
 40 enclosed product.

It is also desirable that the bag serve as a barrier to oxygen and other materials which could cause spoilage of a product wrapped in the film. Furthermore, it is desirable that such a bag be heat shrinkable below the boiling point of water so that high temperatures do not have to be employed to shrink the bag and a convenient heat transfer medium such as hot water can be employed.

45 One successful heat shrinkable bag having a barrier layer of saran is disclosed in US Patent No. 3741253 which issued to H.J. Brax et al. on June 26, 1973. In the Brax patent the multi-ply film has a substrate or sealing layer of cross-linked EVA, a central layer of saran, and an outer or abuse layer of EVA. The inner or sealing layer is referred to as the base or substrate layer. In this instance it is extruded as a tube and is cross-linked and the saran and abuse layer of EVA are extrusion coated thereonto. Thus, a tube
 50 is formed which is thereafter heated to orientation temperature, stretched and then rapidly cooled to form an oriented or heat shrinkable film. Bags are then made by transversely sealing across the tubular structure. Hence, the substrate layer is also the inner layer which is heat sealed to itself to form the seal across the bottom of a bag. The other EVA layer protects the saran from scratches and pin holes and receives the abuse of handling and contact with other packages and surfaces. Hence, it known as the "abuse" layer.

55 As linear copolymers of ethylene known as LLDPE began to become commercially available, they were incorporated into various monolayer and multi-layer structures. In order that the LLDPE layers would extrude more readily and adhere to adjacent film layers, it was found convenient to blend the LLDPE with EVA. Typical patents which disclose layers of LLDPE blended with EVA in a multi-layer, barrier structure

are U.S. Patent No. 3,682,767 which issued on August 8, 1972 to Arthur Wray Britton et al; U.S. Patent No. 4,456,646 which issued to Nishimoto et al on June 26, 1984; U.S. Patent No. 4,495,249 which issued on January 22, 1985 to Ohya et al; U.S. Patent No. 4,424,243 which issued on January 3, 1984 to Nishimoto et al; and, U.S. Patent No. 4,457,960 which issued on July 3, 1984 to David L. Newsome.

One of the primary objects of the present invention is to provide a multi-layer barrier film employing layers of LLDPE in which the adhesion to adjacent saran layers is improved over similar structures in the prior art. In the Britton patent, mentioned above, a copolymer of ethylene with ethylacrylate is mentioned along with the copolymer of ethylene/vinyl-acetate. But no specific example showing the use of ethylene/ethyl-acrylate is given. In Nishimoto '243, mentioned above, the broad term ethylene/alkyl-acrylate is used. But, the only example is, again, ethylene/ethyl-acrylate with a crystalline melting point of 89°C wherein 18% of the copolymer is ethyl-acrylate. In Nishimoto '243 the ethylene/ethyl-acrylate is used only as an unblended adhesive layer. In Ohya '249 the same ethylene/ethyl-acrylate copolymer is used having a melt index of 6 and crystalline melting point of 90°C and 18% by weight of ethyl-acrylate unit. In Ohya '249 the ethylene/ethyl-acrylate copolymer is blended with polyethylene modified by carboxylic acid and used as an adhesive layer.

It is another primary object to employ an ethylene copolymer in a blend with LLDPE or VLDPE to achieve a superior barrier film.

These and other objects are achieved by the invention which is summarized below.

SUMMARY OF THE INVENTION

In one aspect, the present invention is a method of improving the adhesion between a layer of vinylidene chloride copolymer and a layer of a linear ethylene/alpha-olefin copolymer comprising the steps of blending an ethylene/butyl-acrylate copolymer with a linear ethylene/alpha-olefin copolymer; forming a film layer from said blend; and melt joining the layer of said blended copolymers directly to a layer of vinylidene chloride copolymer. The method includes the step of melt joining where the layers are either coextruded or extrusion coated one onto the other. A preferred ethylene/alpha-olefin copolymer for blending with the ethylene/butyl-acrylate is one having a density of less than 0.920 grams per cubic centimeter.

In another aspect, the invention is a multi-layer film having improved adhesion between layers including a layer comprising vinylidene chloride copolymer; and, a blended layer directly joined to the vinylidene chloride copolymer layer, said blended layer comprising 5% to 40% by weight of ethylene/butyl-acrylate copolymer blended with 95% to 60% by weight of linear ethylene/alpha-olefin copolymer.

In still another aspect, the invention is an improvement in making a multi-layer, heat shrinkable, packaging film having a layer comprising a vinylidene chloride copolymer and a layer adjacent thereto comprising a linear ethylene/alpha-olefin copolymer wherein the improvement comprises blending at least 5% by weight of ethylene/butyl-acrylate copolymer in the mixture comprising the linear copolymer layer to improve the adhesion between the two layers.

In yet another aspect, the invention is an improvement in the process of making a heat shrinkable bag constructed from multi-layer thermoplastic film having a barrier layer of vinylidene chloride copolymer and an adjacent layer comprising a linear ethylene/alpha-olefin copolymer wherein the improvement comprises blending at least 5% by weight of ethylene/butyl-acrylate copolymer in the linear copolymer mixture of the adjacent layer thereby improving the adhesion between the adjacent and barrier layers.

The nature, utility and further features of the present invention will be more clearly understood from the following detailed description when read in conjunction with the accompanying drawings.

DESCRIPTION OF THE DRAWINGS

Attached hereto and made a part of this disclosure are drawings in which:

Figure 1 is a graph of the bond strength of a layer of a preferred blend of the present invention and a PVDC layer showing the force required to separate the layers as they are peeled apart;

Figure 2 is a graph similar to Figure 1 except that the layer adjacent to the PVDC layer is a layer of 100% EVA copolymer;

Figure 3 is similar to Figures 1 and 2 except that the layer adjacent to the PVDC layer is a blend of 90% EVA with 10% LLDPE;

Figure 4 is similar to Figures 1-3 except that the layer adhered to the PVDC layer is 93% LLDPE blended with 7% EVA.

DETAILED DESCRIPTION

One method of preparing the film according to the present invention is disclosed in U.S. Patent No. 3,741,253 which issued on June 26, 1973 to Harri J. Brax et al. To prepare the preferred embodiment according to the Brax process, a substrate of ethylene/vinyl-acetate copolymer is extruded as a mono-layer or, if desired, a two-layer film of ethylene/vinyl-acetate copolymer can be coextruded at this point wherein the vinyl acetate copolymer of the ethylene/vinyl-acetate in each layer is different. As the molten film leaves the extruder, it is in the form of a tube which is preferably 3 to 4 inches (76-102 mm) in diameter. This film is cooled, flattened into what is referred to in the art as "tape" and then fed through an irradiation vault to cross-link the material by irradiation. As an alternate, the EVA tape or tubing can be chemically cross-linked in which a well-known chemical cross-linking agent such as one of the peroxides can be included in the blended mixture in the extruder to thereby chemically cross-link the material.

After the cross-linking step is completed, the film is inflated into a tubing and fed through an extrusion coating die which is fed by an extruder. A single layer of saran can be extrusion coated onto the tube at this point or two layers may be extrusion coated onto the substrate, that is, the PVDC layer and the abuse layer can be coextruded and leave the coextrusion die as a two-layer co-extrudate which is then coated onto the inflated substrate as it passes through the die. If this method is not used, then the extrusion coating of a single layer is repeated after the PVDC layer is extrusion coated onto the substrate so that the abuse layer is extrusion coated onto the PVDC layer. In either event, the abuse layer and the PVDC layer are melt joined and contact each other while they are still in a molten or semi-molten state and the contact is made before they have solidified into self-supporting film layers. No adhesive between the PVDC layer and the abuse layer is contemplated by the present invention as it is one of the objects of the present invention to eliminate the necessity for an adhesive layer.

The abuse layer preferably contains 20% ethylene/butyl-acrylate copolymer (EBA) blended in with 80% linear low density polyethylene. The LLDPE or VLDPE, as the case may be, preferably has a density of less than 0.920 and more preferably in the range 0.905 to 0.915. When its density is below 0.910, as defined herein, the linear copolymer is designated as a very low density polyethylene (VLDPE). The ethylene/butyl-acrylate copolymer preferably has a butyl-acrylate content in the range of 2% to 6% and the ethylene/butyl-acrylate copolymer content in the blend can run between 5% and 40% by weight. The density of typical ethylene/butyl-acrylate copolymer runs from 0.921 to 0.923 and melt temperatures are typically 110° C.

After the abuse layer is extruded onto the PVDC layer, the unstretched multi-layer tube is cooled and collapsed and either rolled up into storage or fed immediately into a hot bath where it is brought up to the orientation temperature of the film and biaxially oriented by the trapped bubble technique. The biaxially oriented film is quenched to freeze the molecular orientation and the film is then collapsed and wound up. From this point the film which is now in the form of a stretched, heat shrinkable flattened tube can be longitudinally slit to make sheet film or it can be transversely sealed and severed to make heat shrinkable bags. These heat shrinkable bags by virtue of the gas barrier layer provided by the PVDC layer and by the abuse layer make excellent vacuum bags for the packaging of fresh and processed meats, cheese, poultry, and fish.

Looking now at the drawings, the dramatic increase in bond strength achieved by the present invention will be demonstrated. In Figure 4 a conventional layer of 93% linear low density polyethylene blended with 7% EVA was extrusion coated onto a PVDC layer as the abuse layer and the multi-layer film was biaxially oriented. Subsequently, a one-inch wide sample was cut from the film and with the aid of solvents the PVDC layer was separated from the abuse layer for a distance of slightly more than an inch with the remainder of the sample strip remaining bonded, the separated portions forming grip tabs. After the solvent has been sufficiently dried and removed from the film so that it will not affect the results, one tab was placed in one jaw of an Instron test machine and the other tab in the other jaw. The jaws were then separated and the threshold force to pull the layers apart was recorded and as the jaws continued to move away a tracing was made of the force required to continue the separation. This is what is shown in Figures 1-4. Since the film strip was one-inch wide, the ordinate is reported in pounds per inch. The abscissa is reported in inches which is the separation distance of the jaws.

Looking at Figures 1-4, Figure 1 is a preferred embodiment in which the abuse layer is 80% LLDPE blended with 20% EBA. It will be seen that the bond strength is in the range of 4.2 to 5.0 pounds per inch (735.5-875.6 N/m).

In Figure 2 the abuse layer is 100% ethylene/vinyl-acetate copolymer having 12% vinyl acetate and the bond strength is in the range of 2.7 to 2.3 pounds per inch (472.8-402.8 N/m).

In Figure 3 the abuse layer is 90% EVA blended with 10% LLDPE and the bond strength ranges from 2.2 pounds per inch to 2.7 pounds per inch (385.5-472.8 N/m).

In Figure 4 the abuse layer is 93% LLDPE blended with 7% EVA and the bond strength runs from about 0.25 pounds per inch to 0.7 pounds per inch (43.8-122.6 N/m).

In considering the results of Figures 1-4, it is quite evident that a blend of LLDPE with EBA provides an abuse layer with vastly superior bond strength to the PVDC layer. Such a result is quite surprising and unexpected.

In the following Examples "Dowlex" is a Trade Mark.

Example 1

Example 1 is the film represented in Figure 1 where the abuse layer is 80% LLDPE blended with 20% EBA. The substrate and PVDC layer were prepared according to the Brax et al patent mentioned. The LLDPE was Dowlex brand from Dow Chemical Co. having a density of 0.920 and a melt index of 1.0. The ethylene/butyl-acrylate was Norchem NBA copolymer No. 714 having a density of 0.921 and melt index of 3.2.

Example 2

A second example with a substrate and PVDC layer prepared according to the Brax et al patent used a Dowlex LLDPE resin having a density of 0.917 blended with 15% EBA which is the Norchem 714 resin. An excellent abuse layer resulted having superior bonding strength of approximately 4.5 lbs./in (788 N/m).

Example 3

An abuse layer was prepared from a Dowlex linear copolymer having a density 0.908. About 85% of this resin was blended with 15% of the Norchem 714 with similar surprisingly good results.

The indication is that with lower density LLDPE or VLDPE, i.e., less than 0.920 g/cc and preferably 0.905 g/cc to 0.915 g/cc, the adhesion improvement provided by the ethylene/butyl-acrylate copolymer increases significantly. Also, it is expected that significantly increased adhesion between the blended layer and the saran layer can be achieved by blending 5% to 40% by weight of ethylene/butyl-acrylate into either LLDPE or VLDPE in the blended layer with the optimum range being in the 10% to 25% range.

The work done further indicates that the invention is generally applicable to blends of ethylene/butyl-acrylate with the linear/alpha-olefin copolymers and results of similar nature are to be expected with any of the various vinylidene chloride copolymer resins which are generally designated as saran or PVDC.

EXAMPLE 4

Another example was prepared like the film in Example 1 according to the Brax et al patent, except the 4 layers were as follows:

SUBSTRATE*		(BARRIER) LAYER 3	(ABUSE) LAYER 4
LAYER 1	LAYER 2		
Dowlex 4002 LLDPE (MI = 3.3) (density = 0.912) (comonomer = oct- ene)	75% Dowlex 2045 LLDPE (MI = 1.1) (density = 0.920) (comonomer = octene) 25% EBA (USI Resin 4895, formerly Norchem Resin 714)	PVDC (Dow Resin XU 32027.01) (comonomer = methacrylate)	75% Dowlex 4002 LLDPE (MI = 3.3) (density = 0.912) (comonomer = octene) 25% EBA (USI Resin 4895, formerly Norchem Resin 714)

*The 2-layer substrate was irradiated at 4.5 MR. (1 rad = 1×10^{-2} gray)

As can be seen, this film had a blend layer of ethylene/butyl-acrylate copolymer with a linear ethylene/alpha-olefin copolymer joined directly to each side of the vinylidene chloride copolymer layer.

Claims

1. A method of improving the adhesion between a layer of vinylidene chloride copolymer and a layer of a linear ethylene/alpha-olefin copolymer comprising the steps of:

- a) blending an ethylene/butyl-acrylate copolymer with a linear ethylene/alpha-olefin copolymer;
 - b) forming a film layer from said blend; and,
 - c) melt joining the layer of said blended copolymers directly to a layer of vinylidene chloride copolymer.
- 5
2. The method of claim 1 wherein the step of melt joining the layers is performed by coextruding the two layers.
 3. The method of claim 2 including the step of extrusion coating the two coextruded layers onto a thermoplastic substrate.
 - 10 4. The method of claim 3 including the further step of stretching the substrate and layers coextruded thereonto.
 - 15 5. The method of claim 1 wherein the step of melt joining the two layers is performed by extrusion coating one layer onto the other.
 6. The method of any one of claims 1 to 5 wherein the step of blending includes blending 5% to 40% by weight of the ethylene/butyl-acrylate copolymer with 95% to 60% by weight of the linear ethylene/alpha-olefin copolymer.
 - 20 7. The method of any one of claims 1 to 6 where the ethylene/alpha-olefin copolymer has a density of less than 0.920 gms/cc.
 - 25 8. The method of any one of claims 1 to 7 wherein the ethylene/alpha-olefin copolymer has a density in the range of 0.905 to 0.915 gms/cc, the butyl acrylate content of the ethylene/butyl-acrylate copolymer is in the range from 2% to 6%, and the blending step includes blending 10% to 25% by weight of ethylene/butyl-acrylate copolymer with 90% to 75% by weight of the linear ethylene/alpha-olefin copolymer.
 - 30 9. A multi-layer film comprising:
 - a) a layer comprising vinylidene chloride copolymer; and,
 - b) a blended layer directly joined to the vinylidene chloride copolymer layer, said blended layer comprising 5% to 40% by weight of ethylene/butyl-acrylate copolymer blended with 95% to 60% by weight of linear ethylene/alpha-olefin copolymer.
 - 35 10. The film of claim 9, wherein the vinylidene chloride copolymer layer is joined to a layer comprising a thermoplastic material on its surface opposite the surface joining to the blended layer.
 - 40 11. The film of claim 10 wherein the thermoplastic layer consists essentially of an ethylene/butyl-acrylate copolymer or blends of ethylene/butyl-acrylate copolymers with ethylene polymers or copolymers.
 12. A multi-layer film comprising:
 - a) a layer comprising vinylidene chloride copolymer; and,
 - b) a blended layer directly joined to each side of the vinylidene chloride copolymer layer, each of said blended layers comprising 5% to 40% by weight of ethylene/butyl-acrylate copolymer blended with 95% to 60% by weight of linear ethylene/alpha-olefin copolymer.
 - 45 13. The film of any one of claims 9 to 12 wherein the linear ethylene alpha-olefin copolymer has a density of 0.920 gms/cc or less.
 - 50 14. The film of any one of claims 9 to 13 wherein the butyl acrylate content of the ethylene/butyl-acrylate is in the range of 2% to 6% by weight.
 - 55 15. The film of any one of claims 12 to 14 wherein the vinylidene chloride copolymer layer has methacrylate as its comonomer.
 16. A multi-layer film comprising:

- a) a layer comprising vinylidene chloride copolymer; and
 - b) a blend layer directly joined to each side of the vinylidene chloride layer, one said blend layer (I) being 25% by weight ethylene/butyl-acrylate copolymer with 75% by weight linear low density polyethylene having a density of 0.920 and the other said blend layer (II) being 25% by weight ethylene/butyl-acrylate copolymer with 75% of a linear low density polyethylene having a density of 0.912.
17. A method of making a multi-layer heat shrinkable, packaging film having a layer comprising a vinylidene chloride copolymer and a layer adjacent thereto comprising a linear ethylene/alpha-olefin copolymer, characterised in that at least 5% by weight of ethylene/butyl-acrylate copolymer is blended in the mixture comprising the linear copolymer layer.
18. A method of making a heat shrinkable bag constructed from multi-layer thermoplastic film having a barrier layer of vinylidene chloride copolymer and an adjacent layer comprising a linear ethylene/alpha-olefin copolymer, characterised in that at least 5% by weight of ethylene/butyl-acrylate copolymer is blended in the linear copolymer mixture comprising the adjacent layer.
19. The method of claim 18 including the steps of selecting a linear copolymer for the adjacent layer having a density of less than 0.920 gms/cc and blending 10% to 25% by weight ethylene/butyl-acrylate copolymer having 2% to 6% by weight butyl-acrylate content in 90% to 75% by weight of the linear copolymer.
20. A multi-layer film comprising: (a) a blended layer comprising ethylene/butyl acrylate copolymer blended with linear ethylene/alpha-olefin copolymer; and (b) a layer comprising vinylidene chloride copolymer having one surface thereof directly joined to the blended layer.
21. A multi-layer film according to any one of claims 9 to 16 and 20 wherein the melt temperature of the ethylene/butyl acrylate copolymer is 110 °C.

30 Patentansprüche

1. Verfahren zur Verbesserung der Haftung zwischen einer Schicht aus Vinylidenchlorid-Copolymer und einer Schicht aus linearem Ethylen/α-Olefin-Copolymer, bei dem
 - a) Ethylen/Butylacrylat-Copolymer mit linearem Ethylen/α-Olefin-Copolymer gemischt wird,
 - b) aus dieser Mischung eine Folienschicht gebildet wird und
 - c) die Schicht aus den gemischten Copolymeren direkt mit einer Schicht aus Vinylidenchlorid-Copolymer schmelzverbunden wird.
2. Verfahren nach Anspruch 1, bei dem die Schmelzverbindung der Schichten durch Koextrusion der beiden Schichten erfolgt.
3. Verfahren nach Anspruch 2, bei dem die beiden koextrudierten Schichten auf ein thermoplastisches Substrat extrusionsbeschichtet werden.
4. Verfahren nach Anspruch 3, bei dem das Substrat und die darauf koextrudierten Schichten außerdem gestreckt werden.
5. Verfahren nach Anspruch 1, bei dem die Schmelzverbindung der beiden Schichten durch Extrusionsbeschichtung einer Schicht auf die andere erreicht wird.
6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem in der Mischstufe 5 bis 40 Gew.-% des Ethylen/Butylacrylat-Copolymers mit 95 bis 60 Gew.-% des linearen Ethylen/α-Olefin-Copolymers gemischt werden.
7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem das Ethylen/α-Olefin-Copolymer eine Dichte von weniger als 0,920 g/cm³ besitzt.
8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem das Ethylen/α-Olefin-Copolymer eine Dichte im

Bereich von 0,905 bis 0,915 g/cm³ besitzt, der Butylacrylatgehalt des Ethylen/ Butylacrylat-Copolymers im Bereich von 2 bis 6 % liegt und in der Mischstufe 10 bis 25 Gew.-% Ethylen/Butylacrylat-Copolymer mit 90 bis 75 Gew.-% des linearen Ethylen/ α -Olefin-Copolymers gemischt werden.

- 5 9. Mehrschichtfolie, die
 - a) eine Vinylidenchlorid-Copolymer umfassende Schicht und
 - b) eine direkt mit der Vinylidenchlorid-Copolymerschicht verbundene Mischschicht umfaßt, wobei die Mischschicht 5 bis 40 Gew.-% Ethylen/Butylacrylat-Copolymer gemischt mit 95 bis 60 Gew.-% linearem Ethylen/ α -Olefin-Copolymer umfaßt.
- 10 10. Folie nach Anspruch 9, bei dem die Vinylidenchlorid-Copolymerschicht auf ihrer der mit der Mischschicht verbundenen Oberfläche gegenüberliegenden Oberfläche mit einer ein thermoplastisches Material umfassenden Schicht verbunden ist.
- 15 11. Folie nach Anspruch 10, bei dem die thermoplastische Schicht im wesentlichen aus Ethylen/Butylacrylat-Copolymer oder Mischungen von Ethylen/Butylacrylat-Copolymeren mit Ethylenpolymeren oder -copolymeren besteht.
- 20 12. Mehrschichtfolie, die
 - a) eine Vinylidenchlorid-Copolymer umfassende Schicht und
 - b) an jeder Seite der Vinylidenchlorid-Copolymerschicht eine direkt damit verbundene Mischschicht umfaßt, wobei jede der Mischschichten 5 bis 40 Gew.-% Ethylen/Butylacrylat-Copolymer gemischt mit 95 bis 60 Gew.-% linearem Ethylen/ α -Olefin-Copolymer umfaßt.
- 25 13. Folie nach einem der Ansprüche 9 bis 12, bei der das lineare Ethylen/ α -Olefin-Copolymer eine Dichte von 0,920 g/cm³ oder weniger besitzt.
- 30 14. Folie nach einem der Ansprüche 9 bis 13, bei dem der Butylacrylatgehalt des Ethylen/Butylacrylats im Bereich von 2 bis 6 Gew.-% liegt.
- 35 15. Folie nach einem der Ansprüche 12 bis 14, bei dem die Vinylidenchlorid-Copolymerschicht als Comonomer Methacrylat enthält.
- 40 16. Mehrschichtfolie, die
 - a) eine Vinylidenchlorid-Copolymer umfassende Schicht und
 - b) an jeder Seite der Vinylidenchloridschicht eine direkt damit verbundene Mischschicht umfaßt, wobei eine der Mischschichten (I) aus 25 Gew.-% Ethylen/Butylacrylat-Copolymer und 75 Gew.-% linearem Polyethylen niederer Dichte mit einer Dichte von 0,920 besteht und die andere Mischschicht (II) aus 25 Gew.-% Ethylen/Butylacrylat-Copolymer und 75 % linearem Polyethylen niederer Dichte mit einer Dichte von 0,912 besteht
- 45 17. Verfahren zur Herstellung einer wärmeschrumpfbaren Mehrschichtverpackungsfolie mit einer Vinylidenchlorid-Copolymer umfassenden Schicht und einer daran angrenzenden, lineares Ethylen/ α -Olefin-Copolymer umfassenden Schicht, dadurch gekennzeichnet, daß mindestens 5 Gew.-% Ethylen/Butylacrylat-Copolymer in die Mischung eingemischt werden, die das lineare Copolymer umfaßt.
- 50 18. Verfahren zur Herstellung eines wärmeschrumpfbaren Beutels, der aus einer thermoplastischen Mehrschichtfolie mit einer Sperrschicht aus Vinylidenchlorid-Copolymer und einer angrenzenden, ein lineares Ethylen/ α -Olefin-Copolymer umfassenden Schicht aufgebaut ist, dadurch gekennzeichnet, daß mindestens 5 Gew.-% Ethylen/Butylacrylat-Copolymer in die lineare Copolymermischung eingemischt werden, die die angrenzende Schicht bildet.
- 55 19. Verfahren nach Anspruch 18, bei dem lineares Copolymer mit einer Dichte von weniger als 0,920 g/cm³ für die angrenzende Schicht ausgewählt wird und in 90 bis 75 Gew.-% lineares Copolymer 10 bis 25 Gew.-% Ethylen/Butylacrylat-Copolymer mit einem Butylacrylatgehalt von 2 bis 6 Gew.-% eingemischt werden.
20. Mehrschichtfolie, die (a) Ethylen/Butylacrylat-Copolymer gemischt mit einem linearen Ethylen/ α -Olefin-

Copolymer und (b) eine Vinylidenchlorid-Copolymer umfassende Schicht umfaßt, wobei eine Oberfläche derselben direkt mit der Mischschicht verbunden ist.

21. Mehrschichtfolie nach einem der vorhergehenden Ansprüche, bei der die Schmelztemperatur des Ethylen/Butylacrylat-Copolymers etwa 110° C beträgt.

Revendications

1. Procédé pour améliorer l'adhésion entre une couche de copolymère de chlorure de vinylidène et une couche de copolymère linéaire d'alpha-oléfine éthylène comprenant les étapes consistant à :
 - a) mélanger un copolymère butyle-acrylate éthylène avec un copolymère alpha-oléfine éthylène;
 - b) former une couche de film à partir dudit mélange; et
 - c) assembler par fusion la couche desdits copolymères mélangés directement sur une couche de copolymère de chlorure de vinylidène.
2. Procédé selon la revendication 1, dans lequel l'étape de l'assemblage par fusion des couches est effectuée par la coextrusion des deux couches.
3. Procédé selon la revendication 2, comprenant l'étape de couchage par extrusion des deux couches coextrudées sur un substrat thermoplastique.
4. Procédé selon la revendication 3, comprenant l'étape ultérieure d'étirage du substrat et des couches coextrudées sur celui-ci.
5. Procédé selon la revendication 1, dans lequel l'étape de l'assemblage par fusion des deux couches est effectuée par couchage par extrusion d'une couche sur l'autre.
6. Procédé selon l'une des revendications 1 à 5, dans lequel l'étape de mélange comprend le mélange de 5% à 40% en poids du copolymère butyle-acrylate éthylène avec 95% à 60% en poids du copolymère linéaire alpha-oléfine éthylène.
7. Procédé selon l'une des revendications 1 à 6, dans lequel le copolymère alpha-oléfine éthylène possède une densité inférieure à 0,920 mg/cc.
8. Procédé selon l'une des revendications 1 à 7, dans lequel le copolymère alpha-oléfine éthylène possède une densité dans la gamme de 0,905 à 0,915 gms/cc, la teneur en acrylate de butyle du copolymère butyle-acrylate éthylène est dans la gamme de 2% à 6%, et l'étape de mélange comprend le mélange de 10% à 25% en poids de copolymère butyle-acrylate éthylène avec 90% à 75% en poids du copolymère linéaire alpha-oléfine éthylène.
9. Film multicouche comprenant :
 - a) une couche comprenant un copolymère de chlorure de vinylidène; et
 - b) une couche mélangée assemblée directement à la couche de copolymère de chlorure de vinylidène, ladite couche mélangée comprenant 5% à 40% en poids de copolymère butyle-acrylate éthylène mélangé avec 95% à 60% en poids de copolymère linéaire alpha-oléfine éthylène.
10. Film selon la revendication 9, dans lequel la couche de copolymère de chlorure de vinylidène est assemblée avec une couche comprenant une matière thermoplastique sur sa surface opposée à la surface d'assemblage à la couche mélangée.
11. Film selon la revendication 10, dans lequel la couche thermoplastique est constituée essentiellement d'un copolymère butyle-acrylate éthylène ou de mélanges de copolymères butyle-acrylate éthylène avec des polymères ou copolymères éthylène.
12. Film multicouches comprenant :
 - a) une couche comprenant un copolymère de chlorure de vinylidène; et
 - b) une couche mélangée assemblée directement sur chaque côté de la couche de copolymère de chlorure de vinylidène, chacune desdites couches mélangées comprenant 5% à 40% en poids de

copolymère butyle-acrylate éthylène mélangé avec 95% à 60% en poids de copolymère linéaire alpha-oléfine éthylène.

- 5 13. Film selon l'une des revendications 9 à 12, dans lequel le copolymère linéaire alpha-oléfine éthylène possède une densité de 0,920 gms/cc ou moins.
14. Film selon l'une des revendications 9 à 13, dans lequel la teneur en acrylate de butyle du butyle-acrylate éthylène est dans la gamme de 2% à 6% en poids.
- 10 15. Film selon l'une des revendications 12 à 14, dans lequel la couche de copolymère de chlorure de vinylidène possède du méthacrylate comme comonomère.
16. Film multicouches comprenant :
- 15 a) une couche comprenant un copolymère de chlorure de vinylidène et
b) une couche mélangée directement assemblée sur chaque côté de la couche de chlorure de vinylidène, l'une desdites couches de mélange (I) comprenant 25% en poids de copolymère butyle-acrylate éthylène avec 75% en poids de polyéthylène linéaire de faible densité possédant une densité de 0,920 et l'autre desdites couches mélangées (II) comprenant 25% en poids de copolymère butyle-acrylate éthylène avec 75% d'un polyéthylène linéaire de faible densité possédant une densité de 0,912.
- 20 17. Procédé de réalisation d'un film d'emballage thermorétractable à couches multiples présentant une couche comprenant un copolymère de chlorure de vinylidène et une couche adjacente à celle-ci comprenant un copolymère linéaire alpha-oléfine éthylène, caractérisé en ce qu'au moins 5% en poids du copolymère butyle-acrylate éthylène est mélangé dans le mélange comprenant la couche de copolymère linéaire.
- 25 18. Procédé de réalisation d'un sac thermorétractable réalisé à partir d'un film thermoplastique à couches multiples possédant une couche formant barrière de copolymère de chlorure de vinylidène et une couche adjacente comprenant un copolymère linéaire alpha-oléfine éthylène, caractérisé en ce qu'au moins 5% en poids du copolymère butyle-acrylate éthylène est mélangé dans le mélange de copolymère linéaire comprenant la couche adjacente.
- 30 19. Procédé selon la revendication 18, comprenant les étapes consistant à choisir un copolymère linéaire pour la couche adjacente possédant une densité inférieure à 0,920 gms/cc et à mélanger 10% à 25% en poids de copolymère butyle-acrylate éthylène présentant une teneur de 2% à 6% en poids d'acrylate de butyle dans 90 à 75% en poids du copolymère linéaire.
- 35 20. Film à couches multiples comprenant (a) un copolymère butyle-acrylate éthylène mélangé avec un copolymère linéaire alpha-oléfine éthylène; et (b) une couche comprenant un copolymère de chlorure de vinylidène dont une surface est directement assemblée à la couche mélangée.
- 40 21. Film à couches multiples selon l'une des revendications précédentes, dans lequel la température de fusion du copolymère butyle-acrylate éthylène est environ de 110 °C.
- 45

50

55

FIG.1

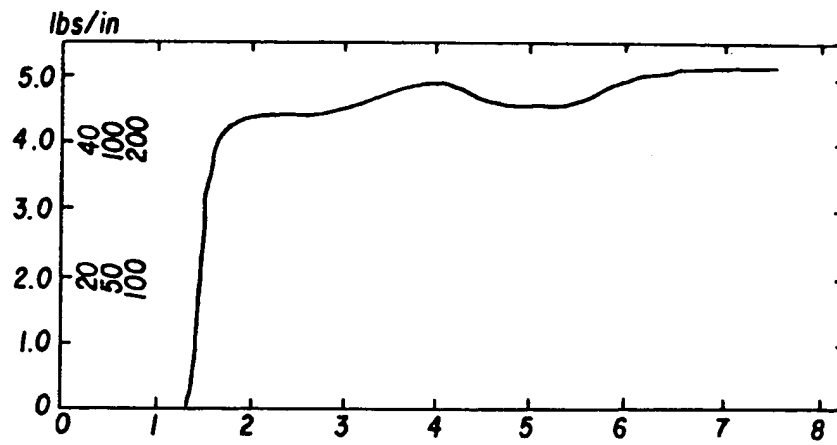


FIG.2

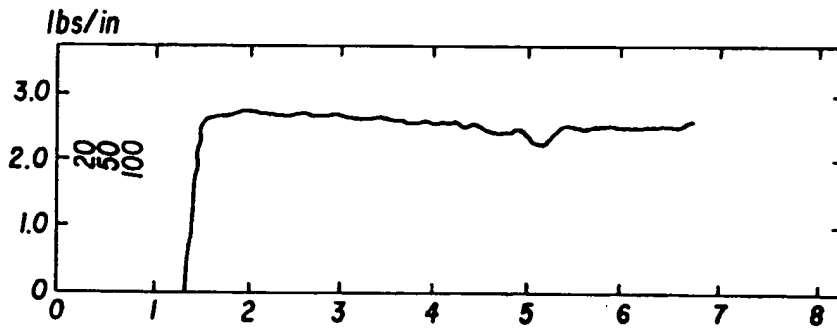


FIG.3

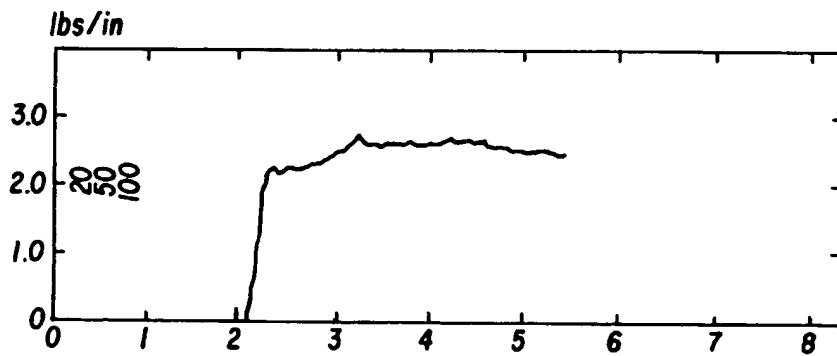
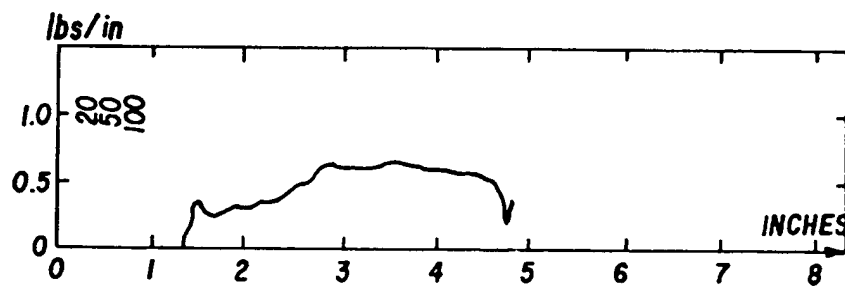


FIG.4



BOND-STRENGTH

INCHES